GC/MS Analysis of PCBs in Waste Oil Using the Backflush Capability of the Agilent QuickSwap Accessory

Application

Environmental

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Abstract

Polychlorinated biphenyls (PCBs) in waste oil are typically analyzed by GC-ECD or GC/MS after solid phase extraction (SPE) cleanup. However, not all problematic matrix components are completely removed during cleanup and are injected into the analytical system, thereby contaminating the column and the detector.

In this application, a practical example of backflushing is presented using the Agilent QuickSwap accessory installed on a 7890 GC/5975 MSD system. Benefits of using QuickSwap instead of the traditional high-temperature bakeout procedure are demonstrated. Column and detector contamination were significantly reduced and sample throughput increased.

Introduction

The determination of polychlorinated biphenyls (PCBs) in mineral oils, including transformer oil, waste oil, or solid waste in general, is a routine application in environmental laboratories. After dilution/dissolution of the oil sample, a solid-phase extraction sample cleanup is used to remove most of the matrix components. Several SPE methods are commonly applied, and some custom cartridges are available specifically for this purpose. According to EN 12766, for instance, a combination of silica and acidified silica/anion exchange ($SiOH$-H_2SO_4/SA) adsorbents is prescribed. The oil samples are diluted and applied to the cartridge in hexane solution and the PCB fraction is then immediately eluted with hexane rinse. The polar matrix compounds remain on the SPE cartridges [1].

In the PCB fraction, however, apolar matrix compounds elute from the cartridge with the PCBs. In one regard, this is not an immediate analytical problem, because when this sample fraction is analyzed by selective detectors like GC-ECD or GC/MS in selected ion monitoring (SIM) mode, the co-extracted solutes are not directly detected. However, their presence contaminates the inlet, column, and detector, causing continuously decreasing system performance. Symptoms such as drifting and increasingly noisy baseline, integration difficulties, decreasing chromatographic resolution, changing column selectivity, and decreasing detector S/N force more frequent inlet system, column, and MS source maintenance and potentially require re-running some samples.

Backflush is a technique that has recently become easier to implement with capillary GC separations due to the availability of Capillary Flow Technology devices [2-9]. One such device is the Agilent QuickSwap, whose primary function is to simplify

changing columns and doing maintenance on GC/MS systems. QuickSwap provides a flow of clean carrier gas that excludes air from the mass spectrometer when columns are disconnected.

An auxiliary electronic pressure control (aux EPC) module or pressure control module (PCM) is typically used to supply the purge gas to QuickSwap and thereby offers the ability to program the pressure during the run. To backflush a capillary column, one need only raise the pressure of QuickSwap (the outlet of the column) higher than that of the inlet (the head of the column). The column flow reverses, eliminating remaining sample components from the head of the column and passing them out of the split vent of the inlet and onto the split vent trap.

Backflushing a column after elution of the compounds of interest is a very effective way of eliminating column contamination. Low-volatility contaminants from the most recently injected sample tend to remain at the head of the column until high oven temperatures are reached. So, by reversing the flow through the column, these contaminants need only flow a short distance to be removed from the column. In the traditional bakeout, they would need to travel through the full length of the column to be removed. In addtion to more effective removal of contaminants, cycle time is significantly reduced, columns are spared from exposure to the high temperatures typical of bakeouts, and detector contamination is reduced.

Sample Preparation

A typical procedure was used to prepare a BCR reference sample (BCR-449, waste mineral oil, high PCB level). A 10% dilution of the oil was made in hexane (1 g in 10 mL). From this solution, 250 µL was applied to a series-combination of two cartridges: a 3 mL cartridge filled with 500 mg of silica treated with H_2SO_4 + 500 mg strong anion exchange resin and a 3-mL cartridge filled with 500 mg silica. The cartridges were preconditioned with hexane. The PCBs were eluted with 4 mL hexane. An aliquot of this solution was used for GC/MS analyses.

GC Conditions

All analyses were performed on an Agilent 7890A GC/5975 MSD system with QuickSwap option number 113 (with Aux EPC module). Injection was done using a 7683 ALS. The GC/MS conditions can be summarized in Table 1:

Table 1. GC/MS System Conditions

Column	30 m x 0.25 mm id × 0.25 µm df	HP-5MS (Agilent P/N 19091-433)
Inlet	S/SI in splitless mode	280 °C, 0.75 min purge delay Purge flow rate: 50 mL/min
Carrier gas Run pressure Backflush pressure	Helium 150 kPa constant pressure 28 kPa	2 mL/min initial flow rate
QuickSwap Restrictor	GC option number 113 or 17 cm × 110 µm id restrictor	Accessory kit G3185B Part number G3185-60363
Column outlet (QuickSwap) Run pressure Backflush pressure	Helium 28 kPa He using AUX EPC 150 kPa	 Through elution of PCBs Held for 5 min after PCBs
Oven temperature program A (no backflush)	50 °C (1 min), 25 °C/min to 200 °C, 10°C/min to 330°C (10 min)	Total run time 30 min
Oven temperature program B (with backflush)	50 °C (1 min), 25 °C/min to 200 °C, 10 °C/min to 300 °C (5 min)	Total run time 22 min
MSD Setpoints	1.5 min solvent delay	260 °C MSD transfer line
SIM/scan settings (AutoTuned)	SIM ions 256, 258, 290, 292, 324, 326, 360, 362, 394, 396 (25 ms dwell time each)	Scan range 40–350 amu

Table 2. Sample Sequence

Run 1	Analysis of waste oil extract by GC/MS in scan/SIM mode – no backflush (oven program A)
Run 2	Blank run – no sample injection, no backflush (oven program A), same as run 1
Runs 3–5	Additional blank runs – same conditions as above (data not shown)
Run 6	Analysis of waste oil extract by GC/MS in scan/SIM mode – with backflush (oven program B)
Run 7	Blank run – no sample injection – same program as in runs 1–5

Results

Total ion chromatograms (TICs) obtained from GC/MS SIM mode are shown in Figure 1 (traditional bakeout with no backflush, A; with backflush, B). The PCBs of interest elute in the 9- to 16-min time range. The profiles obtained by both methods are very similar in PCB resolution and intensity. When these results are carefully scrutinized, little or no difference is noted. However, a clear baseline drop is observed in chromatogram B at 16.5 min, corresponding to the initiation of backflush. In usual backflush methods, the oven temperature ramp and MS data acquisition are stopped when backflush is initiated. In Figure 1B, oven temperature was held at 300 °C, but acquisition was left on to show the drop in baseline when column flow reversed. In contrast to the backflush chromatogram (B), a "hump" is observed extending to 22 min in chromatogram A. This shows the presence of high-boiling matrix interferences in the sample extract and demonstrates the need for removal of these, either through a bakeout or backflush. By the end of the bakeout in 1B, the baseline appears to return to the initial level, indicating that the interferences had been removed.

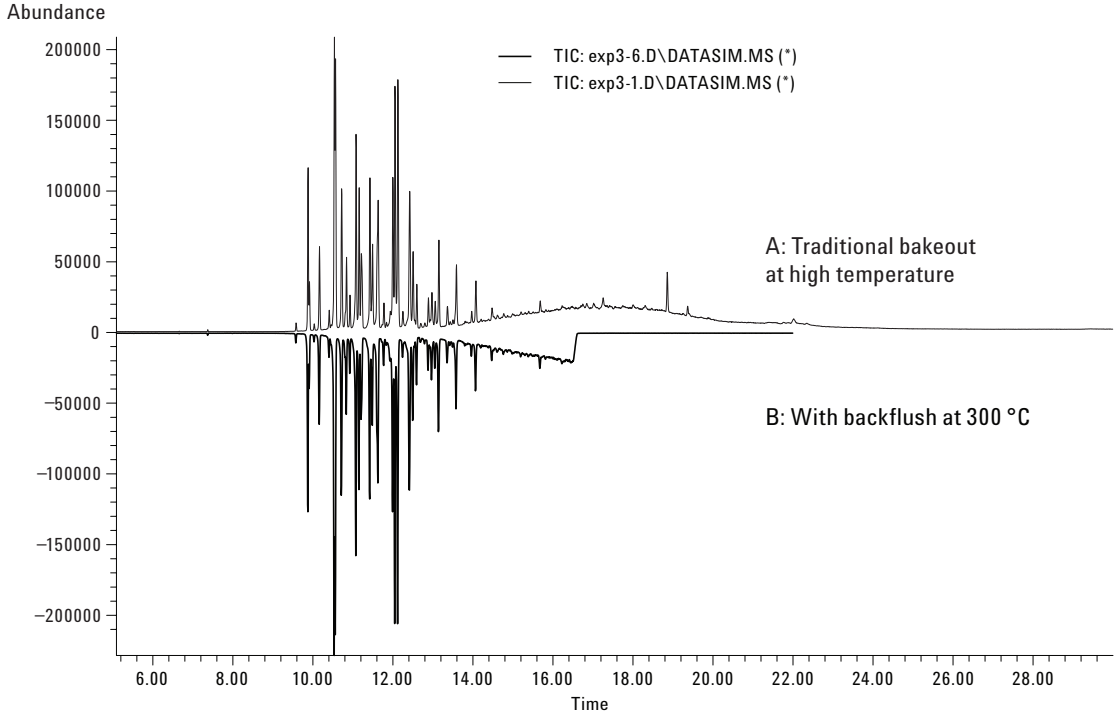

Figure 1. GC/MS total ion chromatograms (TICs) obtained for the analysis of PCBs in waste mineral oil without backflush (A) and with backflush (B)

A helpful recent enhancement of Agilent MSDs is the ability to acquire both SIM and scan data in the same run, termed "simultaneous SIM/Scan." The advantage of simultaneous SIM/Scan is that the benefits of improved detection limits for target compounds with SIM acquisition can be coupled with the benefit of having full-scan data with which to identify unknowns using a library search or spectral interpretation. For the same analytical runs shown in Figure 1 (based on SIM data), total ion chromatograms from full scan data are shown in Figure 2A (no backflush) and Figure 2B (with backflush). The sample matrix interferents can be even more easily seen in these chromatograms. Since all ions in the 40 to 350 amu range are being monitored, the considerable amounts of material eluting after the PCBs of interest dominates the chromatogram. In fact, in the TICs shown in Figure 2, the low-level PCBs are not discernable due to the dominance of the hydrocarbon background. It appears that all the interferents were effectively removed by the bakeout, because the signal returns to baseline even though this was not the case.

To better demonstrate the inferiority of traditional bakeout to backflushing for removing residual components, a blank run (no injection) was made after each of the analytical runs previously shown. The TIC scan-mode chromatogram after sample analysis with bakeout is shown in Figure 3A. To contrast the efficacy of backflush in removing contamination, the blank run done directly after sample analysis with backflush is shown in Figure 3B. In this chromatograph, only signal from normal column bleed was observed. In Figure 3A, the higher level of contamination was seen even after doing the 10 min bakeout at 330 °C and observing the apparent return of signal back to baseline. From this comparison, it is a clear that by relying on a typical bakeout, low-volatility material would continue to build up in the analytical system from run to run, ever increasing the level of background and interfering with subsequent analyses, requiring the column to be prematurely replaced. By backflushing, the low-volatility material was efficiently removed at lower temperatures in less time, while simultaneously lowering source contamination. Column lifetime would improve dramatically. In addition, the backflush method required less cooldown time after the run (from 300 °C instead of 330 °C). Total cycle time was thereby reduced by more than 25% by using backflush.

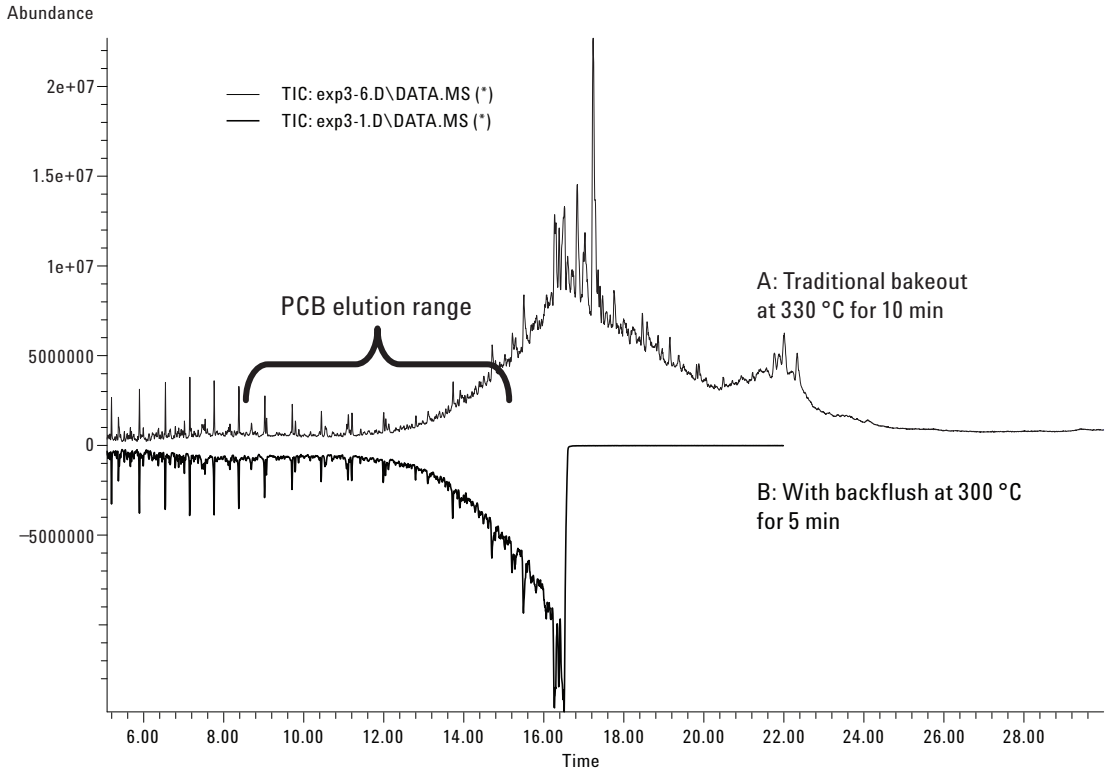

Figure 2. GC/MS TIC scan chromatograms obtained for the analysis of PCBs in waste mineral oil without backflush (A) and with backflush (B).

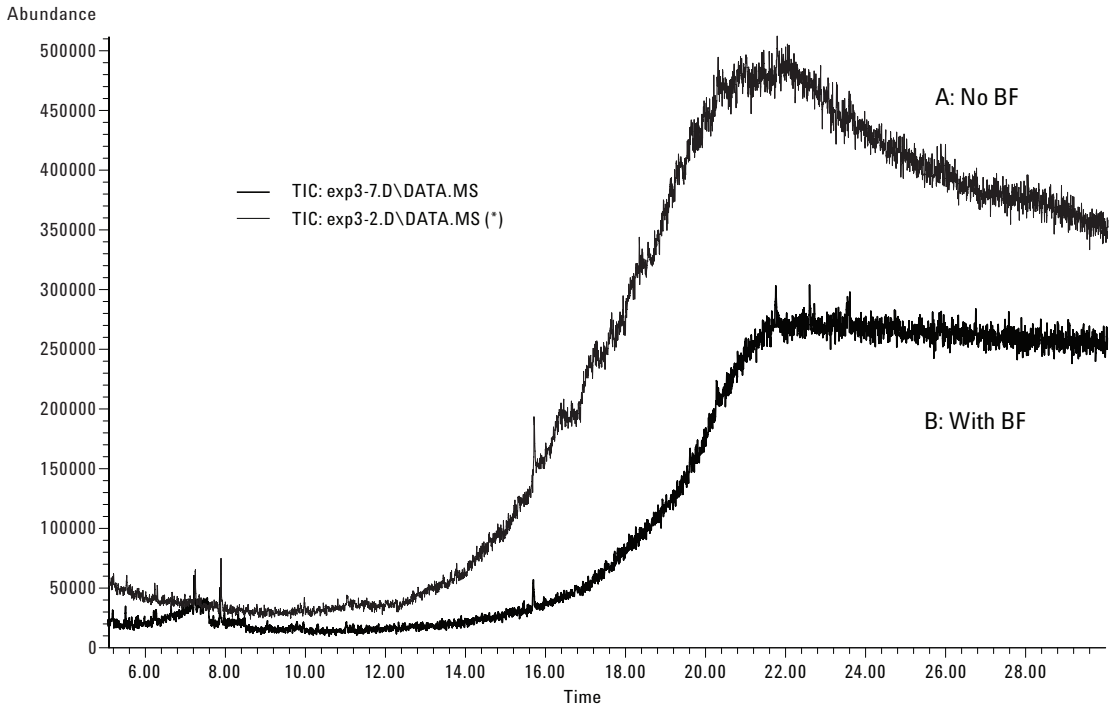

Figure 3. GC/MS TIC chromatograms obtained from scan data for a blank run after the analysis of a sampling with traditional bakeout (no backflush) (A) and with the use of backflush (B).

Conclusion

The benefits from using the backflush capability of QuickSwap on the 7890 GC/MSD were illustrated using an analysis of PCBs in waste mineral oil. The analytical portion of the analysis method was unchanged. There were no negative consequences from adding a backflush to the method. Several advantages were illustrated: improved cycle time, reduced column contamination, improved projected column lifetime, and reduced contamination of the MSD source. Adding backflush to current methods should be seriously considered to increase both laboratory productivity and quality of results.

References

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